SUBSTITUTION REACTIONS AT ANTIMONY

IN THE TETRAPHENYLSTIBONIUM CATION

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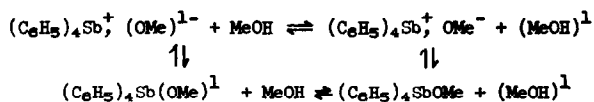
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In the decomposition of quaternary phosphonium alkoxides, stero-
chemical and qualitative rate studies (1) suggest that an alkoxide anion
first adds to the phosphonium cation to form a compound in which the
phosphorus is pentacovalent, and this then loses a suitable anion to give
a new quaternary phosphonium cation in which one of the groups bonded to
phosphorus is an alkoxyl group.  The new cation, in turn, adds a second
alkoxide ion to give a new pentacovalent phosphorus compound in which two
alkoxyl groups are bonded to phosphorus.  Since pentacovalent antimony
compounds are much more stable than pentacovalent phosphorus compounds, it
was thought that the types of intermediates postulated to be formed in the
decomposition of quaternary phosphonium alkoxides could actually be isolated
from reaction systems involving the decomposition of quaternary stibonium
alkoxides.  This turned out to be the case, as described in the following
paragraphs.

Methoxytetraphenylantimony, $(C_6H_5)_4SbOMe$, m.p. 130-132$^O$, was
obtained in 68% yield when tetraphenylstibonium bromide (2) was caused
to react with sodium methoxide in absolute methanol. The NMR spectrum
of the compound in carbon tetrachloride solution showed a singlet at

$\delta$ = 2.74 ppm (with reference to TMS) attributable to the methyl protons
of the methoxyl group. Between $\delta$ = 7.0 ppm and $\delta$ = 8.0 ppm there were
two absorption regions, each about 0.4 ppm wide. The first (and more
strongly absorbing) region had its center at $\delta$ = 7.26 ppm and the second
at $\delta$ = 7.55 ppm, these attributable to the protons of the phenyl groups.
An alkyl to aryl proton ratio of 3:21 was found by integration; expected
ratio for methoxytetraphenylantimony, 3:20. The same compound was
obtained in 97% yield when pentaphenylantimony (3) was refluxed in
absolute methanol solution for 3.5 hr. Benzene was also isolated from
this reaction mixture. This reaction is analogous to the known conversion
of phenyl-bis-biphenyleneantimony to ethoxyphenyl-2-biphenylylbiphenylene-
antimony by the action of refluxing ethanol (4).

The reaction between the tetraphenylstibonium cation and methoxide
ion is evidently a rapid one inasmuch as the NMR spectrum of a fresh
solution of equivalent amounts of tetraphenylstibonium bromide and sodium
methoxide in methanol is identical with that of a methanol solution of
preformed methoxytetraphenylantimony. A solution of tetraphenylstibonium
bromide in methanol gives a completely different spectrum.

It should be pointed out that, whereas a carbon tetrachloride solution
of methoxytetraphenylantimony has a sharp singlet absorption peak at

$\delta$ = 2.74 ppm in its NMR spectrum, this peak is absent in the spectrum of
a methanol solution of methoxytetraphenylantimony. The absorption patterns

in the aromatic region with the two different solvents are very similar
but not identical. A carbon tetrachloride solution has absorption areas
with centers at $\delta = 7.26$ ppm and $\delta = 7.55$ ppm compared with $\delta = 7.38$
and 7.60 ppm for a methanol solution. These results can be explained by
the assumption that equilibria such as the following exist in methanol
solution.

$$(C_6H_5)_4Sb,^+ (OMe)^{1-} + MeOH \rightleftharpoons (C_6H_5)_4Sb,^+ OMe^- + (MeOH)^1$$
$$\updownarrow \qquad\qquad\qquad\qquad \updownarrow$$
$$(C_6H_5)_4Sb(OMe)^1 + MeOH \rightleftharpoons (C_6H_5)_4SbOMe + (MeOH)^1$$

If one or more of these exchange reactions are very rapid, the lack
of any absorption at $\delta = 2.74$ ppm is understandable; rapid chemical
exchange would cause decoupling of the methylenic protons. At the same
time, the nature of the absorption in the aromatic region seems to
indicate that the equilibrium favors the covalent form of the molecule
even in methanol solution.

A covalent structure for crystalline methoxytetraphenylantimony is
consistant with its relatively low m.p. and its ready solubility in non-
polar solvents, such as carbon tetrachloride and petroleum ether. By way
of contrast, tetraphenylstibonium bromide has a m.p. of 214-216° and is
insoluble in these solvents.

When methoxytetraphenylantimony was heated under reflux in absolute
methanol for a period of five weeks, dimethoxytriphenylantimony, m.p.
100-102°, and benzene were obtained in 81% yield. It was also found that
the rate of this reaction is dependent on methoxide ion concentration. In
essentially qualitative experiments, equal amounts of tetraphenylstibonium
bromide were dissolved in equal volumes of methanol containing varying

concentrations of sodium methoxide. As mentioned before, examination of
NMR spectra revealed very rapid formation of methoxytetraphenylantimony.
The solutions were refluxed, and, after convenient periods of time, samples
were withdrawn from the reaction mixtures and NMR spectra taken. Since
the absorption peak of benzene, which appears at $\delta$ = 7.27 ppm, is
sufficiently well separated from the absorption regions of the aromatic
protons of methoxtetraphenylantimony ( $\delta$ = 7.38 and 7.60 ppm) and of the
tetraphenylstibonium cation ( $\delta$ = 7.95 ppm) in methanol solution, it was
possible to observe the increase in benzene concentration as the reactions
progressed. In this way it was convincingly demonstrated that benzene was
produced more rapidly as the concentration of methoxide ion was increased.
Although we feel that the mechanism of this reaction involves formation of
$Na^+$ $(C_6H_5)_4Sb(OMe)_2^-$ as an intermediate which then ejects sodium phenyl,
additional work will have to be carried out before the mechanism is
established with any degree of certainty.

There appears to be little doubt about the covalent nature of
dimethoxytriphenylantimony. It has a low m.p. and sublimes readily. It
is very soluble in nonpolar solvents. The NMR spectra of the compound in
both carbon tetrachloride and methanol solution show a singlet at
$\delta$ = 3.03 ppm, although the singlet is somewhat broader when methanol is
used as the solvent than when carbon tetrachloride is used. Integration
shows the correct ratio of methoxyl hydrogens to aromatic hydrogens.

These results also suggest that dimethoxytriphenylantimony has a
trigonal bipyramidal structure with the methoxyl groups occupying the apical
positions. This would result in the protons of the two methoxyl groups
being equivalent and would account for the singlet peak at $\delta$ = 3.03 ppm.
Another possibility, of course, is simply that the activation energy for

the transition of one space arrangement to another is so low that all
possible forms exist in equilibrium (5). An X-ray crystallographic study
of the compound is presently in progress. Trigonal bipyramidal geometry
has been established for several organoantimony halides (6-9), including
triphenylantimony dichloride and the three trimethylantimony dihalides
(X = Cl, Br, I), and, in each of these, the halogen atoms occupy the apical
positions. Furthermore, there appears to be no pentaco-coordinate
compound, the structure of which is known with certainty, in which the more
electronegative groups do not occupy the apical sites (5).

Dimethoxytriphenylantimony was also prepared by treatment of triphenyl-
antimony dibromide (10) with sodium methoxide in absolute methanol.
Furthermore, dimethoxytriphenylantimony was hydrolyzed to methanol plus
triphenylantimony oxide by the action of an equivalent amount of water
dissolved in acetone (11).

Satisfactory analyses have been obtained for all of the new compounds
mentioned above.

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